COLLISIONAL BROADENING OF THE $J = 7 \leftrightarrow 6$ TRANSITION OF $t$-BUTYL CYANIDE BY CH$_3$CN, OCS, CO$_2$ AND HELIUM

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Experimental studies of the broadening of the absorption line $J = 6 \rightarrow 7$ of (CH$_3$)$_3$CCN due to collisions with the foreign perturbers He, CO$_2$, OCS, and CH$_3$CN have been carried out. The magnitude of the broadening coefficients reflects the type of interactions occurring in the molecular collisions. It has been concluded that the dipole–dipole and dipole–quadrupole interactions are predominant in the (CH$_3$)$_3$CCN admixed with CH$_3$CN and OCS. In the collisions between (CH$_3$)$_3$CCN and CO$_2$ the dipole–quadrupole interactions are present whereas the He perturbed by (CH$_3$)$_3$CCN exhibits dispersive type of interactions.

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1. Introduction

The microwave spectrum of the $t$-butyl cyanide molecule has been described earlier in some papers [1–3] and millimeter-wave spectrum has been worked out by Kisiel [4, 5]. These investigations yield many structural informations in the ground and lowest vibrationally excited states. Principal informations on the dynamical properties of the $t$-butyl cyanide come from pressure broadening measurements [6]. The aim of the present study is to give the qualitative informations on the intramolecular interactions which occur during molecular collisions in $t$-butyl cyanide gas phase.

2. Model

The main source of the broadening of the absorption lines in the microwave frequency band are the collisions between molecules and the intermolecular interactions that occur in these processes. With the knowledge of the pressure broadening coefficient $\Delta \nu / p$ an insight can be gained into the effect of various types of interactions on the linewidth. When foreign gas is used, the linewidth $\Delta \nu$ is

$\Delta \nu = \Delta \nu_1 + \Delta \nu_2$,
where $\Delta \nu_1$ is the self-broadened width and $\Delta \nu_2$ is the partial width due to the foreign gas broadening. When the partial pressure $p_1$ of the absorbing gas is kept constant and the total pressure $p$ is varied by the addition of the foreign gas, then the linewidth $\Delta \nu$ can be calculated from

$$\Delta \nu = C_1 p_1 + C_2 (p - p_1),$$

where $C_1$ and $C_2$ are the self and foreign gas broadening parameters, respectively.

Murphy, Boggs [7, 8] have developed the theory of pressure broadening in which the linewidth is computed using the relation

$$\Delta \nu = \frac{1}{4\pi \tau_i} + \frac{1}{4\pi \tau_f},$$

where $\tau_i$ and $\tau_f$ are the average lifetimes of the initial and final energy levels of the radiating molecule. The average lifetime of the molecule, which is initially found on the level $J_1$, depends on its interactions occurring in the collision process between this molecule and the perturbing one. The interaction can be expressed as a sum of multipole, inductive and dispersive interactions.

The most significant role is played by the dipole–dipole $\mu_1\mu_2/r^3$, dipole–quadrupole, quadrupole–dipole $\mu_iQ_j/r^4$ and quadrupole–quadrupole $Q_1Q_2/r^5$ interactions where $\mu$ and $Q$ are the dipole- and quadrupole moment of the colliding molecules, respectively. Murphy and Boggs [7] define the quadrupole moment of the molecules with an axial symmetry of the charge distribution

$$Q = \sum_i e_i(3z_i^2 - r_i^2).$$

Under the assumption that only the resonant collisions occur, i.e. those in which the total energy change in the system is near zero, the linewidth, according to Murphy and Boggs [7], is proportional to the products $\mu_1\mu_2$ for the dipolar interactions, $\mu_iQ_j$ for the dipole–quadrupole and $Q_1Q_2$ for the quadrupole–quadrupole interactions. However, the approximation of the resonant collisions is not exact in the microwave frequency range and the above classification is bound to be very crude.

3. Experimental

The measurements of the absorption linewidth as a function of the gas pressure were performed using MRR spectrometer with 10 kHz Stark modulation and phase-lock detection [9]. The rotational resonance lines were displayed with slow variation of the klystron frequency.

The linewidth of the rotational transition $J = 6 \Rightarrow 7$ of the pivalonitrile was measured at the frequency $v_0 = 38498.8$ MHz. Both the frequency $v_0$ and the linewidth were calibrated within to $\pm 15$ kHz using the frequency counter model YaZTch-51.

The study was made at the pure pivalonitrile [6] and the pivalonitrile with four different admixtures. The gas pressure was measured with the absolute manometer to an accuracy $\pm 1.0$ millitorr. The pressure of the pivalonitrile gas in the sample cell was set constant in the range from 5 to 15 mTr, then the admixture gas was introduced thus increasing the pressure from 0 to 40 mTr.
The effects of the Doppler broadening, saturation, Stark modulation and the collisions of the gas molecules with the cavity walls were accounted for [6] in the determination of the linewidth. The least squares fit was used in the calculation of the pressure broadening coefficient.

4. Results

The pivalonitrile molecule is an axial symmetric top with the rotational constant $B = 2749.9096$ MHz [1, 4, 5] and the dipolar moment $\mu = 3.95$ D [1]. The large value of the dipole moment effects a large intensity of the rotational absorption lines $\alpha = 1.18 \times 10^{-5}$ cm$^{-1}$.

At low frequencies the structure of the rotational spectrum due to the centrifugal forces remains unresolved. Namely, the components corresponding to the different $K$-values of the $J = 6 \Rightarrow 7$ transition span between 0.053 and 0.601 MHz. With this magnitude of the separation the $K$-components remain unresolved and a single broadened absorption line is observed. For the $J = 6 \Rightarrow 7$ transition the pressure broadening coefficient $\Delta \nu/p$ of the pure pivalonitrile and the gas admixed with He, CO$_2$, OCS and CH$_3$CN was measured. The linewidths as a function of the gas pressure are shown in Fig. 1.

![Fig. 1. Linewidth versus pressure for (CH$_3$)$_3$CCN $-$ J = 7 $\Leftarrow$ 6 line (o) perturbed by He (full triangles), OCS (A), CO$_2$ (+), CH$_3$CN (•).](image)

The values of the pressure broadening coefficient of the pure and admixed pivalonitrile are collected in Table. Table gives also the results of linewidth calculations using Murphy–Boggs theory [7, 8]. We take into account dipole–dipole, dipole–quadrupole and dispersion interactions. We have calculated the linewidth
coefficients of $K = 0 \div 6$ components of the $J = 6 \Rightarrow 7$ line and used it for the determination of the envelope linewidth.

Perturbed states up to $J_2 = 50$ have been considered with a correction term for all states $J_2 > 50$.

Table

<table>
<thead>
<tr>
<th>Perturber</th>
<th>Piv</th>
<th>CH$_3$CN</th>
<th>OCS</th>
<th>CO$_2$</th>
<th>He</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \nu/p_{exp}$</td>
<td>76.9</td>
<td>38.4</td>
<td>8.7</td>
<td>14.6</td>
<td>4.6</td>
</tr>
<tr>
<td>$\Delta \nu/p_{cal}$</td>
<td>57.00</td>
<td>54.61</td>
<td>13.08</td>
<td>13.24</td>
<td>9.6</td>
</tr>
</tbody>
</table>

5. Conclusions

The above results allow to study the effect of various types of interactions on the linewidth. For the mixture of pivalonitrile and CH$_3$CN the main effect comes from the dipole–dipole and dipole–quadrupole interactions ($\mu_{\text{CH}_3\text{CN}} = 3.913$ D [11] and $Q_{\text{CH}_3\text{CN}} = 1.8$ DÅ [10, 14]). The pivalonitrile and OCS mixture is similar ($\mu_{\text{OCS}} = 0.715$ D [11] and $Q_{\text{OCS}} = 5.58$ DÅ [12]). The dipole–quadrupole interaction is most important in the collision process of carbon dioxide molecules ($Q_{\text{CO}_2} = 8.6$ DÅ [13]) while in the collisions of helium atoms the dispersive interactions play the most important role.

Comparing the results of Table one concludes that the largest $\Delta \nu/p$ value is reached when there are large dipole moments, e.g. pivalonitrile and acetonitrile and the dipolar interaction prevail. On the other hand, in the OCS, exhibiting a small dipole moment, the value of $\Delta \nu/p$ coefficient is much lower. The large value of the broadening coefficient $\Delta \nu/p$ observed in the pivalonitrile and CO$_2$ mixture may result from the large value of the quadrupole moment of the latter.

The comparison of the experimental and theoretical results shows that the agreement between the two is poor in case where strong dipole–dipole interactions (large dipolar moment) are responsible for the line broadening.

References

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